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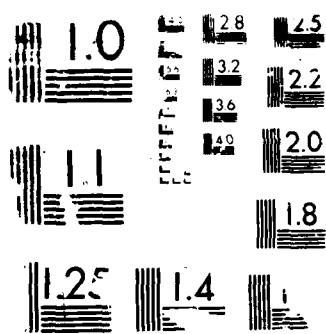
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SOOT OXIDATION KINETICS

FINAL REPORT

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U.S. ARMY RESEARCH OFFICE

CONTRACT NO. DAAG29-83-C-0023

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <i>Soot and carbon black oxidation kinetics have been measured under controlled temperature, pressure, and oxygen concentration, [O₂], conditions in a modified High Temperature Fast Flow Reactor over the range 1000-1700 K and 0.05 ≤ [O₂] ≤ 200 × 10¹⁶ cm⁻³. The kinetic measurements are carried out under conditions where the carbon particle consumption rate is controlled by gas particle interactions and not by mass transfer. Auxiliary surface area measurements on partially oxidized particles collected from the HTFFR indicate that the oxidation is controlled by external surface rather than</i>		

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pore-centered reactions. The measured particle reactivities ($\text{g cm}^{-2} \text{ s}^{-1}$) are $\times 10$ smaller than predicted by the often used Nagle-Strickland-Constable semiempirical model for carbon oxidation nor do the $[\text{O}_2]$ dependences conform to this model. Additional work is required to elucidate the reasons for this disparity.



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STATEMENT OF THE PROBLEM STUDIED

The objective of this research program was to measure oxidation rate constants (reactivities) for soot and soot-like carbon particles at temperatures between 1000 and 2000 K. Such measurements have been carried out over the temperature range 1000-1700 K for the O_2 oxidation of three carbon blacks (soot-like materials) and soots collected from an ethylene/air diffusion flame. A modified AeroChem High Temperature Fast Flow Reactor (HTFFR) was used for most of the reactivity measurements. Additional preliminary measurements were made of the oxidation of soot in static, bulk sample experiments at temperatures as low as 740 K.

SUMMARY OF IMPORTANT RESULTS

The most important result of the HTFFR measurements is the finding that the measured reactivities do not conform to the widely accepted Nagle and Strickland-Constable (NSC) expression¹ developed from the two-site oxidation mechanism of Eyring and coworkers.² Neither the magnitudes nor the $[O_2]$ dependences of the measured reactivities follow the predictions of the NSC formulation. It was speculated that the presence of large amounts of sulfur impurity in the carbon blacks studied might have been the cause of this anomalous behavior, but studies with "sulfur-free" soots did not support this conjecture while still showing disagreement with NSC predictions. It may be that the lower temperature range covered in these HTFFR studies than those generally used in the prior shock tube and flame studies of carbon particle oxidation (e.g., Refs. 3-6) is connected with this disagreement, but further work is needed to explore both this possibility and the effects of sulfur on the observed reactivities.

The physical and chemical properties of the carbon particles studied in this work are presented in Table I and illustrate the wide range of particle compositions and sizes studied. The carbon blacks were obtained commercially; two soots from the C_2H_4 /air flame were used, one of which was "clean" while the other was contaminated with ≈ 0.5 wt.% Zn (the form of the Zn in the particles was not determined). The measured reactivities, R_p ($g\ cm^{-2}\ s^{-1}$), are presented in Table II along with their $[O_2]$ dependences. In each case, an extremely wide range of $[O_2]$ was covered to determine the order of the reaction in $[O_2]$, and in each case, only a single fractional order was found, rather than the change from first to zero order in $[O_2]$ predicted from the two-site mechanism. No major effect of the Zn contamination of the C_2H_4 /air soot was found on the oxidation rate.

In Table III and Fig. 1, the temperature dependences of the reactivities are illustrated for oxidation in "air" (20% O_2 , 80% N_2) at 101 kPa (1 atm). Under this condition, both the soot and carbon black oxidations exhibit similar activation energies of 120 - 140 $kJ\ mol^{-1}$, consistent with previous measure-

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ments (see, e.g., Ref. 7). Calculations indicate that for the range of particle sizes utilized in this work, mass transport (diffusion) of O₂ to the particle surface is rapid compared to the observed reaction rates. Thus, the observed reactivities are controlled by the gas-particle reaction rate. Separate surface area measurements (by N₂ gas adsorption with BET analysis) of partially oxidized particles collected from the HTFFR showed that the oxidation kinetics are well described by the simple "shrinking sphere" model in which a fully dense carbon particle undergoes external surface oxidation with concomitant decrease in radius. This is taken to indicate that particle porosity effects on the observed reactivities are negligible. Oxidation rate determinations (measured by weight loss per unit time) on bulk soot samples at 740 K in air (101 kPa) were made as a function of percentage of previous oxidation. The results show a small (< 25%) increase in the rate of oxidation as the fractional oxidation of the particles increases from 0 to 85%, perhaps indicating an increase in active surface area^a with oxidation. The bulk oxidation reactivities at 740 and 950 K shown in Table II should be considered as preliminary values.

The main kinetic measurements were carried out in a uniquely modified AeroChem High Temperature Fast Flow Reactor (HTFFR). Part of the modifications involved development of a particle feed system for delivering stable flows of particle-laden diluent gas to the heated reactor in which these flows were mixed with O₂ and additional diluent. The reaction time was controllable from 30-800 ms and oxygen concentrations between $\approx 1 \times 10^{15}$ and 2×10^{18} cm⁻³ were used. The extent of reaction was measured by gas chromatography (gc) by determining the amount of CO + CO₂ produced for a given reaction condition. Carbon mass flow was also determined by gc by completely oxidizing the particles flowing into the HTFFR and measuring the CO + CO₂ produced. The apparatus, technique, and results of carbon black oxidation studies are fully described in the publication listed below.

PUBLICATION

"Oxidation Kinetics of Carbon Blacks over 1300-1700 K," W. Felder, S. Madronich, and D.B. Olson, submitted to Energy & Fuels.

PRESENTATIONS

"Soot Oxidation Kinetics," W. Felder, presented at 7th ARO/Engine Fuels Workshop, Wayne State University, 13-14 October 1987.

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"Oxidation Kinetics of Carbon Blacks over 1300-1700 K," W. Felder, and S. Madronich, presented at Fuel Division Symposium, Fall ACS Meeting, New Orleans, LA, 30 August-4 September 1987.

"Soot Oxidation Kinetics," W. Felder, D.B. Olson, and S. Madronich presented at 6th ARO/Engine Fuels Workshop, Davis, CA, 17-18 March 1986.

"Soot Oxidation Kinetics," W. Felder, S. Madronich, and D.B. Olson, presented at Fall Technical Meeting, Eastern Section: The Combustion Institute, Philadelphia, PA, 4-6 November 1985.

"Soot Oxidation Kinetics," W. Felder, D.B. Olson, and S. Madronich presented at 5th ARO/Engine Fuels Workshop, Philadelphia, PA, 27-28 March 1984.

PERSONNEL

AeroChem personnel who contributed to this project were W. Felder, S. Madronich, D.B. Olson, R.J. Gill, D.G. Keil, H.F. Calcote, and L. Aldridge. No degrees were awarded.

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TABLE I
PHYSICAL AND CHEMICAL PROPERTIES OF CARBON PARTICLES

<u>Carbon Particle</u>	<u>Mean Particle Diam (nm)</u>	<u>BET (N₂) Surface Area (m²/g)</u>	<u>Volatiles (wt. %)</u>	<u>Metal Content^c (wt. %)</u>	<u>Ash (wt. %)</u>	<u>Sulfur (wt. %)</u>
Raven 16 ^a (R16), Carbon Black	61	25 (29 ^b)	0.9	0.1	0.27	1.67
Conductex SC ^a (CSC), Carbon Black	20	220 (190 ^b)	1.5	0.08	0.49	0.85
Raven 850 ^a (R850), Carbon Black	31	70 (72 ^b)	--	0.04	0.28	1.31
Soot (C ₂ H ₄ /Air)	--	105 ^b	5.8 ^b	0.01 ^b	0.04 ^b	< 0.02 ^b
Soot (C ₂ H ₄ /Air + Zn)	--	108 ^b	5.7 ^b	0.6 ^b	0.14 ^b	< 0.02 ^b

^a Data supplied by manufacturer, Columbian Chemical Co.

^b Properties measured in this work.

^c The measured metallic impurities contents (wt.%) are summarized below:

<u>Metallic Impurity</u>	<u>R16^a</u>	<u>CSC^a</u>	<u>R850^a</u>	<u>Soot^b</u>	<u>Soot + Zn^b</u>
Σ Mn, Mg, Al, Ti	0.007	0.008	0.002	0.007	0.030
Fe	0.045	0.005	0.003	0.005	0.051
Na	0.021	0.047	0.029	< 10 ⁻⁵	0.032
Ca	0.025	0.016	0.006	< 10 ⁻³	< 10 ⁻³
Zn	< 10 ⁻⁸	< 10 ⁻⁸	< 10 ⁻⁸	< 10 ⁻⁵	0.5

TABLE II

EXTERNAL SURFACE REACTIVITY^a R_e FOR CARBON PARTICLE OXIDATION BY O_2
 $\log_{10} R_e = \log_{10} R_0 + n \log_{10} [O_2]$

Carbon Particle	T (K)	$\log_{10} R_0$		[O_2] range (10^{16} cm $^{-3}$)
		[O_2] $^{-n}$)	n	
Raven 16 (Carbon Black)	1300	-16.3 ± 0.6 ^b	0.62 ± 0.04 ^b	0.2 - 158
	1400	-16.5 ± 2.0	0.64 ± 0.12	2.0 - 104
	1470	-16.1 ± 1.3	0.66 ± 0.10	0.05 - 98
	1580	-14.9 ± 1.7	0.59 ± 0.10	0.12 - 177
	1680	-15.1 ± 1.0	0.61 ± 0.07	0.18 - 154
Conductex SC (Carbon Black)	1410	-18.6 ± 0.5	0.76 ± 0.13	0.04 - 200
	1580	-18.8 ± 1.1	0.82 ± 0.17	0.2 - 132
	1650	-14.2 ± 1.4	0.57 ± 0.08	0.3 - 75
Raven 850 (Carbon Black)	1550	-15.3 ± 2.1	0.62 ± 0.20	0.08 - 52
	1400	-16.6 ± 1.7	0.65 ± 0.15	0.9 - 61
	1300	-16.0 ± 1.5	0.60 ± 0.15	1.0 - 95
Soot ^c (C ₂ H ₄ /Air)	1400	-16.1 ± 1.1	0.66 ± 0.05	0.1 - 120
	1200	-20.2 ± 1.0	0.85 ± 0.10	0.1 - 170
	1000	-21.6 ± 2.2	0.85 ± 0.25	0.5 - 180
Soot ^c (0.5% wt. Zn) (C ₂ H ₄ /air)	1400	-16.3 ± 1.2	0.65 ± 0.11	0.1 - 100
	1200	-10.5 ± 2.2	0.80 ± 0.22	0.5 - 87
	1000	-21.9 ± 1.5	0.88 ± 0.30	1.0 - 50
		<u>$\log_{10} R_e$</u>		
Soot ^c (C ₂ H ₄ /air)	950	- 8.6 ± 1.0	d	155
	740	-10.5 ± 1.0	d	200

^a g cm $^{-2}$ s $^{-1}$; gas concentration units, molecules cm $^{-3}$

^b One standard deviation

^c Soot collected from ethylene/air diffusion flame.

* Measured at a single [O_2].

TABLE III
 REACTIVITIES OF CARBON PARTICLES IN AIR (20% O₂, 80% N₂)
 AT 101 kPa FROM HTFFR MEASUREMENTS
 Reactivity (g cm⁻² s⁻¹)

T (K)	Carbon Blacks			Soots ^a	
	Raven 16	Conductex SC	Raven 850	C ₂ H ₄ /Air	C ₂ H ₄ /air + 0.5% Z
1680	6.9 × 10 ⁻⁵	---	---	---	---
1650	---	1.1 × 10 ⁻⁴	---	---	---
1580	5.5 × 10 ⁻⁵	7.9 × 10 ⁻⁵	---	---	---
1550	---	---	7.1 × 10 ⁻⁵	---	---
1470	6.0 × 10 ⁻⁵	---	---	---	---
1400	1.1 × 10 ⁻⁵	1.2 × 10 ⁻⁵	1.2 × 10 ⁻⁵	6.3 × 10 ⁻⁵	2.6 × 10 ⁻⁵
1300	7.8 × 10 ⁻⁶	---	6.9 × 10 ⁻⁶	---	---
1200	---	---	---	1.6 × 10 ⁻⁵	1.0 × 10 ⁻⁵
1000	---	---	---	6.3 × 10 ⁻⁷	1.2 × 10 ⁻⁶

^a Soot collected from ethylene/air diffusion flame.

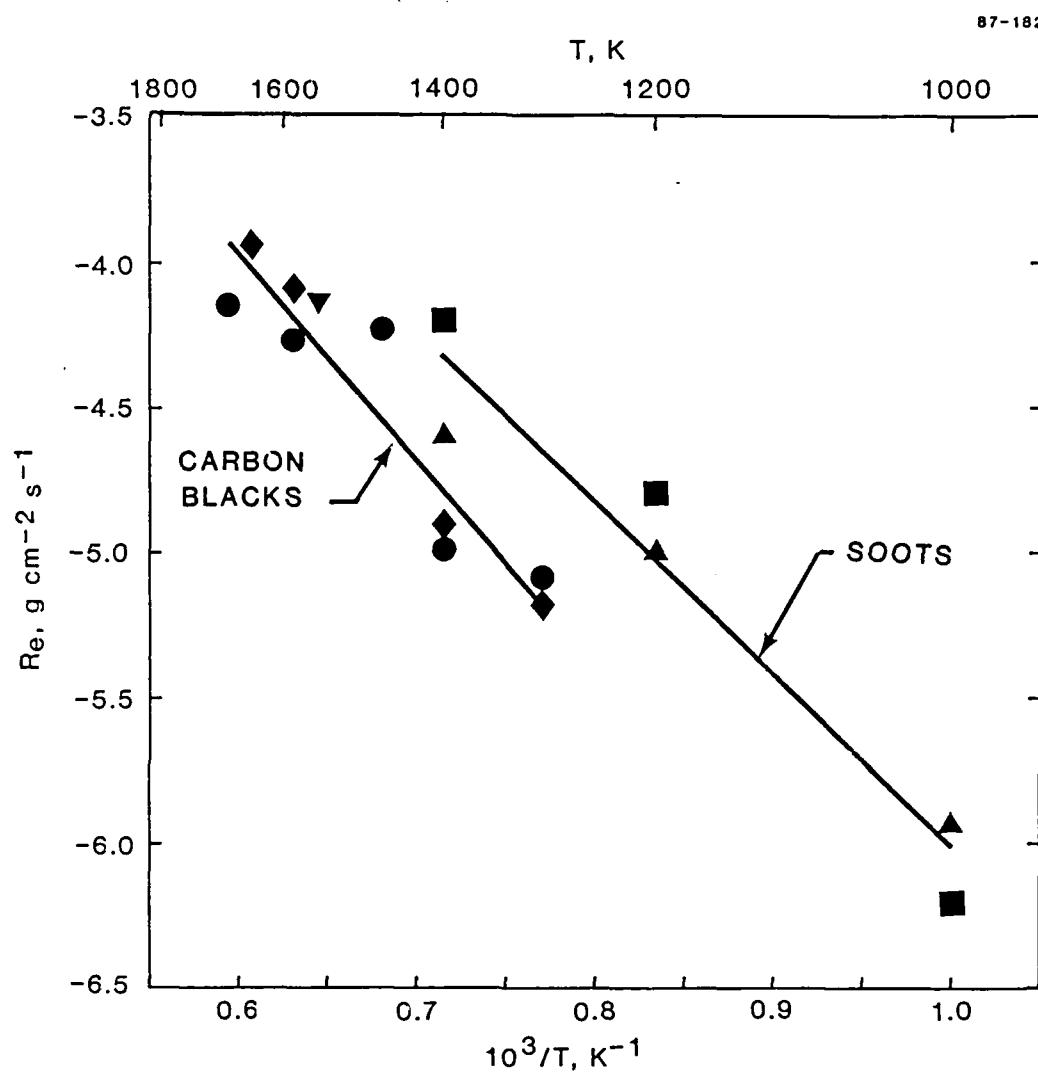


FIGURE 1 REACTIVITIES OF CARBON PARTICLES ABOVE 1000 K
IN AIR (20% O₂, 80% N₂) AT 101 kPa (1 atm)

- Carbon Black, Raven 16; ◆ Carbon Black, Conductex SC;
- ▼ Carbon Black, Raven 850; ■ Soot, Ethylene/Air Flame;
- ▲ Soot + 0.5% (wt.) Zn, Ethylene/Air Flame

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